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A Methano-Bridged Dehydro[24]annulenedione. A Highly Diatropic Dicationic 22π-Electron Species in D_2SO_4

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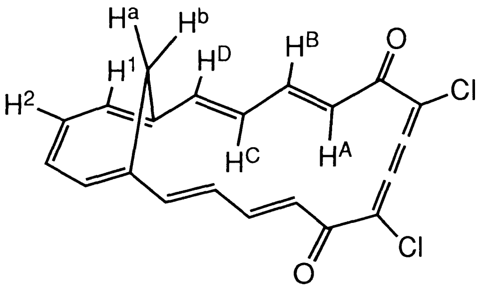
A methanodehydro[24]annulenedione with a 1,4-dichlorobutatriene moiety was synthesized. The compound formed a highly stable dicationic species in D_2SO_4, which showed the strongest diatropicity hitherto reported for 22π-electron aromatic systems.

We recently reported that an intramolecular oxidative coupling of a diacetylenic diketone **2** under Glaser conditions afforded unexpectedly a methanodehydro[20]annulenedione **1** with a 1,4-dichlorobutatriene moiety. Dissolution of **1** in D_2SO_4 afforded a stable dark orange solution, whose ^1H NMR spectrum showed extremely strong diatropicity, suggesting the formation of a highly delocalized 18π-electron dicationic species **1a**.1) The diatropicity of **1a** exceeds that of the 14π-electron dicationic species **3** derived from a monocyclic [16]annulenedione reported by Lombardo and Sondheimer,2) as judged from the chemical shift differences between the inner and outer olefinic protons. Both the methano-bridge and the butatriene moiety



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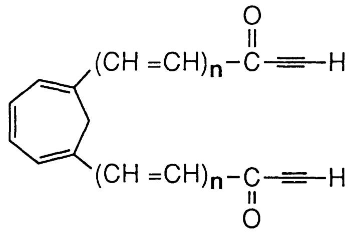
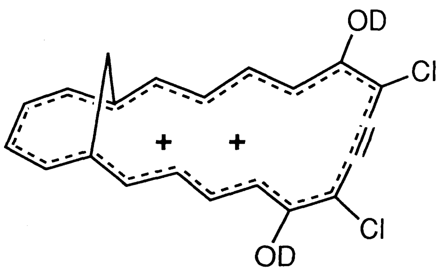
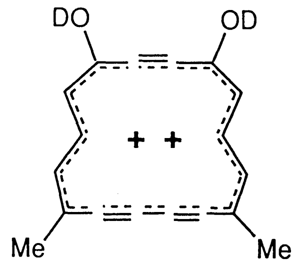


2 : n=2
5 : n=3



1a



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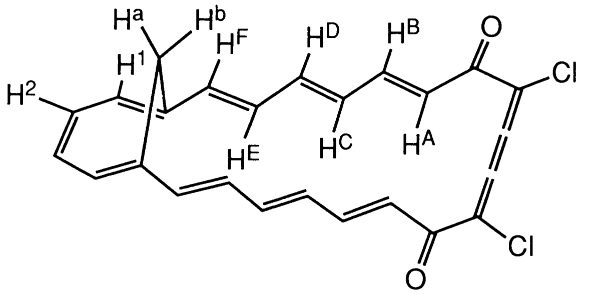

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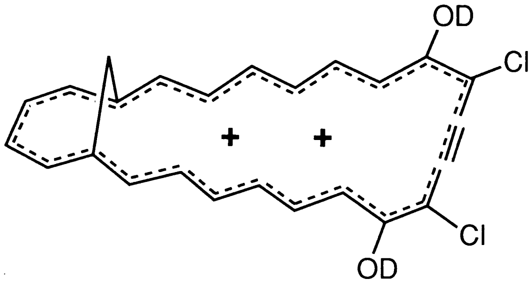


4a

would play important roles to keep the molecular skeleton of **1** highly planar and suitably rigid and thus to render the system highly diatropic. These interesting findings have prompted us to attempt the preparation of higher homologs of **1** and to study their tropic properties.

In this paper we report the synthesis of the methano[24]annulenedione **4** and the even stronger diatropicity of the corresponding dicationic species in D_2SO_4 than that of **1a**, which apparently contradicts the hitherto observed tendency that tropicity decreases as the ring size becomes larger.

Bisethynylation of 1,6-bis(6-formyl-1,3,5-hexatrienyl)-1,3,5-cycloheptatriene$^{3)}$ (45% yield) followed by oxidation of the resulting diol with $Ba(MnO_4)_2$ (68% yield) afforded the diacetylenic diketone **5**.$^{4)}$ A Glaser coupling was performed by bubbling oxygen through a mixture of compound **5**, copper(I) chloride, and ammonium chloride in aqueous ethanol-benzene containing conc. HCl at 60-65 °C,$^{5)}$ similarly to the preparation of **1**.$^{1)}$ Chromatography of the product on silica gel afforded the dichloromethanodehydro[24]annulenedione **4**,$^{6)}$ a higher homolog of **1** with two additional CH=CH groups, as dark green needles, mp 232-236 °C (dec), in 10% yield.$^{7)}$

The ^1H NMR spectral data of **4** in $CDCl_3$ are given in Table 1 together with those of compound **1**. The chemical shift differences $\Delta\delta^{BC}$ between H^B and H^C as the representatives of the outer and inner olefinic protons, respectively, are also shown, which are regarded as an approximate measure of the magnitude of the ring current induced. The $\Delta\delta^{BC}$ values are ca. 1.5 ppm and rather similar between **1** and **4**, suggesting that both **1** and **4** are only slightly diatropic in $CDCl_3$ by polarization of the two carbonyl groups. Chemical shifts of the methano-bridge protons are also very similar between the two compounds and their average positions are ca. 0.5 ppm higher than those of the acyclic precursors **2** and **5**.

Dissolution of compound **4** in D_2SO_4 afforded a dark violet solution, suggesting the formation of a dicationic species. The solution was very stable and remained unchanged for several months at -10 °C, although the solution in $CDCl_3$ was less stable and considerably decomposed in several days at -10 °C. The ^1H NMR spectral data in D_2SO_4 are also compiled in

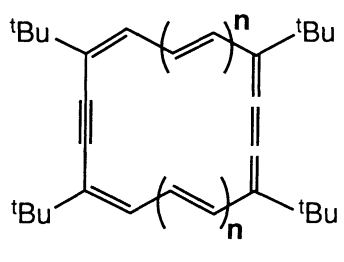
Table 1. ^1H NMR (500 MHz) data, δ (J/Hz), of compounds **1** and **4** at 26 °C[a)]

Compound	**1**[b)]		**4**	
Solvent	$CDCl_3$	D_2SO_4	$CDCl_3$	D_2SO_4
H^A	6.15 d (14.5)	-4.39 d (13.2)	6.10 d (14.6)	-6.48 d (13.3)
H^B	7.68 dd (14.5,11.5)	11.00 t (12.7)	7.74 dd (14.6,11.6)	11.58 t (13.0)
H^C	6.27 dd (15.4,11.5)	-2.74 t (13.3)	6.00 dd (14.6,11.6)	-4.73 t (12.9)
H^D	7.06 d (15.4)	10.92 d (14.0)	7.05 dd (14.5,11.1)	11.13 t (12.6)
H^E			6.29 dd (15.6,11.0)	-4.25 t (13.1)
H^F			6.84 d (15.3)	11.21 d (13.6)
H^1	6.72 m	9.52 bm	6.62 m	9.62 bm
H^2	6.98 m	9.72 bm	6.90 m	9.98 bm
CH_2 a	1.27 d (13.4)	-3.18 d (14.2)	1.29 d (13.2)	-4.30 bs
b	3.06 d (13.4)	-2.68 d (14.2)	3.12 d (13.2)	-3.52 bs
$\Delta\delta^{BC}$/ppm	1.41	13.74	1.74	16.31

a) d: doublet; dd: double doublet; t: triplet; m: multiplet; bm; broad multiplet; bs: broad singlet. b) Ref. 1.

Table 1. The olefinic protons inside the ring, H^A, H^C, and H^E, as well as the methano-bridge protons appear at an extremely high field of δ -3—-7, while the olefinic protons outside the ring appear at a very low field of δ 9—12, indicating the induction of very strong diamagnetic ring current due to the extensively delocalized 22π-electron species **4a**. The $\Delta\delta^{BC}$ value amounts to 16.3 ppm, which considerably exceeds that of compound **1** in D_2SO_4 (13.7 ppm). Also the methano-bridge protons in **4a** appear at a higher field than that of **1a** by ca. 1 ppm.[8)]

This finding is remarkable in two aspects. Such large diatropicity as observed in **4a** for a 22π-electron system has never been observed not only in diprotonated annulenediones[9)] and protonated annulenones[10)], but also in neutral annulenes, such as the carbocyclic 'acetylene-cumulene' bisdehydroannulenes **6**[11)] and the methanobisdehydroannulenes **7**.[3,12)] The second aspect is that **4a**, a 22π-electron system, is even more diatropic than **1a**, an 18π-electron system. This observation is also unprecedented. It has been recognized that the diatropicity decreases as the ring size increases in peripherally conjugated systems such as **6** and **7**.[3,11)] The apparent anomaly observed in the



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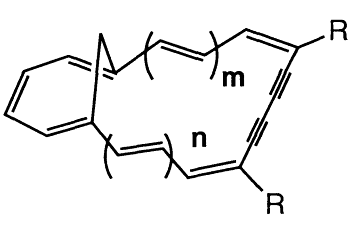

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present study may at least partly be ascribed to the lower planarity of **1a** than **4a** due to the ring strain, as judged from inspection of molecular models. The methano-bridge protons of **4a** appear as two broad peaks at 26 °C, because the flipping of the methano-bridge through the average plane of the macrocycle takes place on the NMR time-scale, while those of **1a** appear as a distinct pair of doublets indicating the far slower conformational change. This may support the lower planarity of **1a** than **4a**.

Further studies including the synthesis of higher homologs of **4** are in progress.

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7) Found: C 71.05; H, 4.44%. Calcd for $C_{25}H_{18}Cl_2O_2$: C 71.26; H, 4.30%.
8) UV-vis of **4a** (H_2SO_4) λ_{max} 345 (sh, ε 49300), 485 (sh, 70600), 505 (76500), 540 (sh, 75200), 590 (67400), 789 (7100), 815 (8400), 887 nm (22300). The UV spectra of **1a** and **4a** are similar in shape and bathochromic shifts of the maxima by 60—100 nm are observed on going from **1a** to **4a**, suggesting the higher delocalization of π-electrons in **4a** than in **1a**, in accordance with the NMR spectral behavior.
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